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## (54) PRODUCTION OF AMINES FROM ALCOHOLS

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known from UK Patent 679,014 and U.S. Patent 3,022,349 that amines can be prepared by reaction of alcohols with ammonia using copper catalysts. The reaction is however very incomplete and sometimes requires an afteramination over a nickel catalyst. Moreover, mainly dialkylamines are formed.

According to another method described in U.S. Patent 3,151,115, catalysts of nickel, cobalt, copper, manganese, chromium, molybdenum and thorium are used for the production of amines and polyamines. The disadvantage of this method is the high proportion of N-disubstituted amines in the amines formed. Thus for example in addition to ethylene diamine, a considerable proportion of undesired piperazine is obtained from ethanolamine. The same is true of German Printed Application 1,170,960 where Raney nickel is used as catalyst.

It is furthermore known from UK Patent 833,589 that oxides of nickel, cobalt or copper or mixtures of the same may be used as catalysts in the production of amines from alcohols. This method has the disadvantage that a very large amount of piperazine is obtained and very high temperatures are necessary.

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We have now found that the reaction of an alcohol with a stoichiometric excess of ammonia or a primary or secondary amine at elevated temperature and superatmospheric pressure in the presence of hydrogen and a hydrogenation catalyst containing elemental cobalt, nickel and copper gives very good yields of the corresponding amine when the catalyst used is a supported catalyst which contains (calculated on the cobalt plus nickel plus copper content of the catalyst) from 70 to 95% by weight of a mixture of cobalt and nickel and from 5 to 30% by weight of copper, the weight ratio of cobalt to nickel being within the range from 4:1 to 1:4.

It is preferred to use a weight ratio of cobalt to nickel of from 2:1 to 1:2, particularly of 1:1 and a copper content of from 10 to 20% by weight, particularly 15% by weight, based on the cobalt plus nickel plus copper content in the catalyst.

The catalyst used in the process according to the invention may also contain, based on the copper plus nickel plus cobalt content (100 parts by weight) of the catalyst, up to 20 parts by weight of up to two of the metals manganese, chromium, zinc, vanadium and silver, these metals being present in elemental form or in the lowest valence state obtainable with hydrogen reduction.

The catalyst may also contain based on the metal content (100 parts by weight) of the catalyst and calculated as phosphorus pentoxide or boron trioxide, up to 20 parts by weight of phosphoric acid or boric acid or a mixture of the two or the correspond-

ing oxides or their salts, or, based on the metal content (100 parts by weight) of the catalyst, up to 20 parts by weight of alkali metals, for example sodium or potassium, or alkaline earth metals, for example calcium or barium.

The abovementioned additives which may be present in the catalyst in addition to cobalt, nickel and copper are advantageously present in amounts up to 10 parts by weight, particularly 1 to 2 parts by weight, based upon the metal content (100 parts by weight) of the catalyst.

Reaction between the alcohol and the ammonia or amine is carried out in the presence of hydrogen and in the presence or absence of water. It may suitably be carried out at a temperature of from 100° to 250°C and a hydrogen partial pressure of from 10 to 250 atmospheres, particularly from 20 to 200 atmospheres.

Preferred starting materials are alkanols having one to eighteen carbon atoms, for example ethanol, propanol, butanol, pentanol, hexanol, 2-ethylhexanol, tridecanol and stearyl alcohol; cycloalkanols having five to twelve carbon atoms such as cyclohexanol; alkanolamines, for example ethanolamine, propanolamine, isopropanolamine, hexanolamine, diethanolamine and diisopropanolamine; or polyalcohols, particularly diols, having one to fifteen carbon atoms, for example ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, 4,4'-bishydroxycyclohexylpropane-(2,2), or their monoethers, for example methyl glycol, ethyl glycol, butyl glycol; or polyalkylene glycol ethers, for example polyethylene glycol ethers, polypropylene glycol ethers and polybutylene glycol ethers.

When ammonia is used as the second reactant, primary amines are obtained. Primary amines may also be used as reactants and then secondary amines are obtained. When secondary amines are used, the corresponding tertiary amines are obtained. Preferred primary and secondary amines have alkyl radicals having one to twelve carbon atoms or cycloalkyl radicals having 5 to 7 carbon atoms and optionally substituted by alkyl groups having one to eight carbon atoms as substituents.

Examples of suitable amines are methylamine, dimethylamine, ethylamine, diethylamine, propylamine, butylamine, amylamine, hexylamine and cyclohexylamine. The ammonia or amine is used in a stoichiometric excess with reference to the alcohol. It is preferred to use from 5 to 50 moles, advantageously from 10 to 40 moles, particularly 20 to 30 moles of ammonia or amine per mole of amino group to be introduced. Hydrogen is suitably supplied in an amount of from 5 to 100 liters per mole of alcohol

component, particularly from 10 to 30 liters per mole of starting material.

The process according to the invention may also be carried out in the presence of water, for example from 1 to 50% by weight based on the alcohol component.

The catalyst is applied to a carrier, for example aluminum oxide or silicon dioxide. The metal content of the catalyst is advantageously from 5 to 80% by weight, particularly from 10 to 30% by weight, based on the whole catalyst.

Copper and the mixture of cobalt and nickel are advantageously used in the ratio from 1:19 to 1:3 in the catalyst. The other metals (manganese, chromium, silver, zinc or vanadium) or the acids (phosphoric acid or boric acid) or the alkali metals (sodium or potassium) or the alkaline earth metals (calcium or barium) are advantageously used in the ratio from 1:200 to 1:10 to the mixture of cobalt and nickel.

The catalysts may be prepared for example by precipitating the metal components (with or without the said acids or their salts) as such or onto a powdered carrier, from their salts in aqueous solution, for example with sodium carbonate or sodium hydroxide, or the precipitate may be applied to such a carrier, the composition washed until neutral and then dried at elevated temperature, for example at temperatures of from 60° to 180°C; the composition is made into moldings such as tablets or pellets and heated for some time at elevated temperature, such as 300° to 800°C, in a muffle furnace. Phosphoric acid and boric acid can also be used in the form of their salts, or of their pyro- or poly-anions or salts thereof, for the production of the catalyst and/or can be present in such forms in the already-prepared catalyst. Prior to use, the catalyst is reduced with hydrogen, preferably at temperatures of from 220° to 300°C.

Other catalysts containing cobalt, nickel and copper are obtained for example by adding aqueous solutions of the nitrates of cobalt, nickel and copper, with or without the nitrates of the said other metals and the inorganic acids or their salts, to the preformed solid carrier and then heating the resultant impregnated catalyst to 300° to 800°C in a muffle furnace.

The reaction of the alcohol with ammonia or amine may be carried out without any solvent. It may be advantageous however to use the reaction discharge as a solvent.

The process according to the invention may be carried out batchwise. It is advantageous to carry it out continuously. This method will now be described by way of example. A mixture of one of the said alcohols and a stoichiometric excess of ammonia or an amine is fed together with recycled reaction discharge into the top of a vertical

high pressure tube which is filled with a catalyst of the said composition. The feed may also be made hydraulically up from the bottom. At the same time hydrogen is metered in. The said conditions of pressure and temperature are maintained during the reaction. Ammonia or amine is removed from the reaction discharge which is then subjected to fractional distillation to isolate the desired amine.

Amines obtainable by the process according to the invention are suitable for the production of emulsifiers, plant protection agents and vulcanization accelerators.

The following Examples illustrate the invention. The parts given in the following Examples are parts by weight. They bear the same relation to parts by volume as the kilogram to the liter.

#### EXAMPLE 1

A vertical high pressure tube having a capacity of 500 parts by volume is filled with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide and 4% by weight of copper oxide on aluminum oxide. After the catalyst has been reduced with hydrogen at 250°C, there are metered in per hour at the top of the high pressure tube 100 parts of ethanolamine and 350 parts by volume of liquid ammonia, a temperature of 160°C being maintained. At the same time a pressure of 300 atmospheres gauge is maintained by forcing in hydrogen. Ammonia is distilled off from the reaction discharge. 115 parts per hour of a mixture is obtained which according to gas chromatographic analysis (calculated anhydrous) contains 49% of ethylenediamine, 36% of ethanolamine, 6% of piperazine and 8% of polyamines. The yield of ethylenediamine after a single pass is thus 77% based on reacted ethanolamine.

#### EXAMPLE 2

A vertical high pressure tube having a capacity of 500 parts by volume is filled with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide, 4% by weight of copper oxide and 0.2% by weight of phosphoric acid (calculated as  $P_2O_5$ ) on aluminum oxide. Under experimental conditions as described in Example 1, 113 parts per hour of a mixture is obtained which according to gas chromatographic analysis and calculated anhydrous contains 44% of ethylenediamine, 46% of ethanolamine, 3% of piperazine and 5% of polyamines. The yield of ethylenediamine after a single pass is thus 82% with reference to reacted ethanolamine.

#### EXAMPLE 3

A vertical high pressure tube having a capacity of 500 parts by volume is filled

with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide and 4% of copper oxide on aluminum oxide. After the catalyst has been reduced with hydrogen at 250°C, 100 parts per hour of an 80% aqueous hexanediol-(1,6) solution and 350 parts by volume of liquid ammonia are metered in at the top of the high pressure tube, a temperature of 220°C being maintained. A pressure of 300 atmospheres gauge is maintained at the same time by forcing in hydrogen. Ammonia is distilled off from the reaction discharge. 115 parts per hour of a mixture is obtained which according to gas chromatographic analysis and calculated anhydrous contains 49% of hexamethyleneimine, 23% of hexamethylenediamine, 7% of 1-aminohexanol-(6), 4% of hexanediol-(1,6), 9% of N-amino-hexylhexamethyleneimine and 5% of polyamines. After the hexamethyleneimine has been separated, the remainder may be returned to the reactor.

#### EXAMPLE 4

A vertical high pressure tube having a capacity of 2000 parts by volume is filled with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide, 4% by weight of copper oxide and 0.2% by weight of phosphoric acid (calculated as  $P_2O_5$ ) on aluminum oxide. After the catalyst has been reduced with hydrogen at 250°C, an hourly feed of 500 parts by volume of a 10% solution of 4,4'-bishydroxycyclohexylpropane-(2,2) in liquid ammonia is supplied to the top of the high pressure tube, a temperature of 220°C being maintained. A pressure of 300 atmospheres gauge is maintained at the same time by forcing in hydrogen. Ammonia is distilled off from the reaction discharge. 53 parts per hour of a mixture is obtained which according to gas chromatographic analysis (calculated anhydrous) contains 3% of 2-cyclohexyl-2-(4-aminocyclohexyl)-propane, 87% of 4,4'-bisaminocyclohexylpropane-(2,2), 6% of 4,4'-bishydroxycyclohexylpropane-(2,2) and 3% of residue. The yield of 4,4'-bisaminocyclohexylpropane-(2,2) after a single pass is thus 92% with reference to 4,4'-bishydroxycyclohexylpropane-(2,2).

#### EXAMPLE 5

A vertical high pressure tube having a capacity of 500 parts by volume is filled with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide, 2% by weight of copper oxide and 0.5% by weight of manganese oxide. After the catalyst has been reduced with hydrogen at 250°C, 50 parts per hour of diethanolamine and 350 parts by volume of liquid ammonia are metered in at the

top of the high pressure tube, a temperature of 160°C being maintained. A pressure of 300 atmospheres gauge is maintained by forcing in hydrogen at the same time. Ammonia is distilled off from the reaction discharge. 58 parts per hour of a mixture is obtained which according to gas chromatographic analysis (calculated anhydrous) contains 4% of ethylenediamine, 22% of piperazine, 17% of N-(β-aminoethyl)-ethanolamine, 54% of diethanolamine and 1% of polyamines.

#### EXAMPLE 6

A vertical high pressure tube having a capacity of 500 parts by volume is filled with a catalyst which contains 10% by weight of cobalt oxide, 10% by weight of nickel oxide, 4% by weight of copper oxide and 0.4% by weight of phosphoric acid (calculated as  $P_2O_5$ ). After the catalyst has been reduced with hydrogen at 250°C, 100 parts of polypropylene glycol (molecular weight about 1400) and 350 parts by volume of liquid ammonia are metered in per hour at the top of the high pressure tube, a temperature of 180°C being maintained. A pressure of 300 atmospheres gauge is maintained at the same time by forcing in hydrogen. Ammonia is distilled off from the reaction discharge. 102 parts per hour of a product is obtained which, calculated anhydrous, has an amine number of 76. This is conversion of 95%.

#### WHAT WE CLAIM IS:—

1. A process for the production of an amine by reaction of an alcohol with a stoichiometric excess of ammonia or a primary or secondary amine at elevated temperature and superatmospheric pressure in the presence of hydrogen and a hydrogenation catalyst containing elemental cobalt, nickel and copper, wherein a supported catalyst is used which contains, based on the cobalt plus nickel plus copper content of

the catalyst, from 70 to 95% by weight of a mixture of cobalt and nickel and from 5 to 30% by weight of copper, the ratio by weight of cobalt to nickel being from 4:1 to 1:4.

2. A process as claimed in claim 1 wherein the catalyst used also contains, based on the cobalt plus nickel plus copper content (100 parts by weight) of the catalyst, up to 20 parts by weight of one or two of the metals manganese, chromium, zinc, vanadium and silver as elements or in the lowest state of valency obtained with hydrogen reduction.

3. A process as claimed in claim 1 or 2 wherein the catalyst used also contains, based on the metal content (100 parts by weight) of the catalyst, and calculated as phosphorus pentoxide or boron trioxide up to 20 parts by weight of phosphoric acid or boric acid or a mixture thereof or oxides or salts thereof.

4. A process as claimed in any of claims 1 to 3 wherein the catalyst used also contains, based on the metal content (100 parts by weight) of the catalyst, up to 20 parts by weight of an alkali metal or an alkaline earth metal.

5. A process as claimed in any of claims 1 to 4 carried out at temperatures of from 100° to 250°C.

6. A process as claimed in any of claims 1 to 5 wherein a hydrogen partial pressure of from 10 to 250 atmospheres is maintained.

7. A process as claimed in claim 1 carried out substantially as described in any of the Examples.

8. Amines when obtained by the process claimed in any of claims 1 to 7.

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